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## Chlorinated volatile organic compounds (CVOCs) and 1,4-dioxane kinetics and equilibrium adsorption studies on selective macrocyclic adsorbents

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### Abstract

Chlorinated volatile organic compounds (CVOCs) are often found in combination with 1,4-dioxane which has been used as a solvent stabilizer. It would be desirable to separate these compounds since biodegradation of 1,4-dioxane follows an aerobic pathway while anaerobic conditions are needed for biodegrading CVOCs. Conventional adsorbents such as activated carbon (AC) and carbonaceous resins have high adsorption capacities for 1,4-dioxane and CVOCs but lack selectivity, limiting their use for separation (Liu et al., 2019). In the current work, two macrocyclic adsorbents,  $\beta$ -CD-TFN and Res-TFN, were examined for selective adsorption of chlorinated ethenes in the presence of 1,4-dioxane. Both adsorbents exhibited rapid adsorption of the CVOCs and minimal adsorption of 1,4-dioxane. Res-TFN had a higher adsorption capacity for CVOCs than  $\beta$ -CD-TFN (measured linear partition coefficient,  $K_d$  2140–9750 L·kg<sup>-1</sup> versus 192–918 L·kg<sup>-1</sup> for 1,1, DCE, cis-1,2-DCE and TCE, respectively) and was highly selective for CVOCs (TCE  $K_d$  ~117  $K_d$  for 1,4-dioxane). By comparison, TCE and 1,4-dioxane adsorption on AC was approximately equal at 100  $\mu\text{g}\cdot\text{L}^{-1}$  and approximately 1/3 of the adsorption of TCE on the Res-TFN. The greater adsorption and selectivity of Res-TFN suggest that it can be used as a selective adsorbent to separate CVOCs from 1,4-dioxane to allow separate biodegradation.

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Appendix A. Supplementary data

The following is the supplementary data to this article:

CRediT authorship contribution statement

**Elham Abaie:** Writing – original draft, Software, Investigation. **Manish Kumar:** Investigation. **Uriel Garza-Rubalcava:** Methodology, Validation, Writing – review & editing. **Balaji Rao:** Methodology. **Yilang Sun:** Investigation. **Yuexiao Shen:** Writing – review & editing, Supervision. **Danny Reible:** Conceptualization, Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2024.100520.

## Keywords

Selective adsorption; CVOCs; 1,4-dioxane;  $\beta$ -CD-TFN; Res-TFN; Rapid adsorption; Linear isotherms; Partition coefficient; TCE; Activated carbon; Biological degradation

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## 1. Introduction

Chlorinated volatile organic compounds (CVOCs) are commonly used in various industries and consumer products. CVOCs' high mobility and volatility result in their migration to groundwater, air, and soil, posing a threat to human health. Additionally, 1,4-dioxane, which is classified as a probable human carcinogen by US EPA, coexists with chlorinated solvents in the environment (Aoyagi et al., 2018; Mahendra et al., 2013). While established biological methods exist for remediating chlorinated solvents (Field & Sierra-Alvarez, 2004) or 1,4-dioxane individually (Shu et al., 2017), bioremediation of a mixture of these compounds is challenging due to several reasons. CVOCs and 1,4-dioxane are biodegradable by both anaerobic and aerobic metabolisms. However, anaerobic metabolism is preferred for CVOCs since the carbon atoms in highly chlorinated VOC's, have a relatively high oxidation state. Moreover, anaerobic biodegradation is effective in environments with low redox potential, where oxygen is limited or absent. This makes it suitable for treating CVOC-contaminated sites that may have anaerobic conditions, such as groundwater or certain subsurface environments (Barajas Rodriguez, 2016; Mahendra et al., 2020). In contrast, aerobic biodegradation is preferred for 1,4-dioxane for several reasons. Aerobic biodegradation processes exhibit faster degradation rates compared to anaerobic processes. This can lead to more rapid and efficient removal of 1,4-dioxane from the contaminated environment. Moreover, aerobic conditions support a wider range of microorganisms that can utilize 1,4-dioxane as a carbon and energy source (Aoyagi et al., 2018; Ramalingam & Cupples, 2020; Shen et al., 2008). Therefore, there is a critical need to separate 1,4-dioxane from chlorinated solvents in order to achieve an effective bioremediation approach.

Previous studies have investigated different adsorbents, such as granular activated carbon (GAC), carbonaceous resins, and minerals like zeolites, to combine adsorption and bioremediation for enhanced removal of target chemicals (Chen et al., 2019; Liu et al., 2019; Mahendra et al., 2013; Mohr, 2010; Shu et al., 2017). However, these adsorbents lack selectivity, and competitive adsorption of CVOCs hampers the biodegradation of 1,4-dioxane. Hence, it is essential to develop adsorbents with higher selectivity to facilitate the separation and subsequent biodegradation of 1,4-dioxane and CVOCs.

The objective of the current research is to separate 1,4-dioxane from CVOCs using selective macrocyclic materials that can enhance bioremediation. Macrocyclic adsorbents, particularly  $\beta$ -cyclodextrin ( $\beta$ -CD) and its derivatives, have garnered significant attention.  $\beta$ -CD is characterized by hydrophobic inner surface which allows hydrophobic interactions to play a key role in adsorption mechanism. Moreover, due to their unique geometry,  $\beta$ -CD adsorbents form host-guest complexes inside their hydrophobic cavity with contaminants of similar sizes (Crini & Morcellet, 2002). We hypothesized that, given the difference in

hydrophobicity between CVOCs and 1,4-dioxane,  $\beta$ -CD adsorbents would exhibit higher affinities toward CVOCs and facilitate their separation from 1,4-dioxane.

To explore the competitive adsorption of CVOCs in the presence of 1,4-dioxane and to understand the impact of electrostatic and hydrophobic interactions in the adsorption mechanisms, we examined functionalized  $\beta$ -CD adsorbents with various crosslinkers. The presence of seven -OH groups on  $\beta$ -CD enables functionalization (Folch-Cano et al., 2014). Three different crosslinkers, namely epichlorohydrin (EPI), hexamethylene diisocyanate (HDI), and tetrafluoroterephthalonitrile (TFN), were employed to modify  $\beta$ -CD polymer with hydroxyl, amine, and fluorine-based groups, respectively.  $\beta$ -CD-EPI and  $\beta$ -CD-HDI were examined as more conventional  $\beta$ -CD adsorbents, while  $\beta$ -CD-TFN, a more recent adsorbent, was also included.  $\beta$ -CD-EPI, which lacks significant functional groups in its structure, was chosen to assess any competitive adsorption of CVOCs in presence of 1,4-dioxane. Mean while,  $\beta$ -CD-HDI, which contains amine groups, was selected to investigate the impact of electrostatic interactions in the adsorption of CVOCs. Additionally,  $\beta$ -CD-TFN was synthesized through the nucleophilic aromatic substitution of  $\beta$ -CD hydroxyl groups. The presence of aromatic groups increases the porosity and surface area of this adsorbent (Peixiao Tang, 2018). We hypothesized that the incorporation of numerous fluorine groups in its polymeric structure and the resulting enhanced hydrophobicity would improve the adsorption of CVOCs and facilitate their separation from 1,4-dioxane. Although  $\beta$ -CD adsorbents have been extensively used for adsorbing a range of organic pollutants, they appear ineffective in removing halomethanes due to the large cavity size. Recent research has focused on developing adsorbents with permanent porosity and high surface area to effectively capture these compounds. Polymers composed of resorcinarene receptors crosslinked with TFN (Res-TFN) and tetrafluoroisocyanonitril (Res-TFIN) have been shown to absorb halomethanes and 1,4-dioxane separately (Skala et al., 2019). However, previous studies have not explored the efficacy of these polymers in selective removal of halomethanes in the presence of 1,4-dioxane. While both Res-TFN and Res-TFIN illustrated adsorption of halomethanes and 1,4-dioxane individually, Res-TFN showed lower removal of 1,4-dioxane. Since in this study selective adsorption of CVOCs was targeted, we chose Res-TFN to investigate its selective adsorption of CVOCs in presence of 1,4-dioxane. The Res-TFN polymer, characterized by its high porosity and surface area due to the presence of numerous aromatic groups indicates a heightened affinity for hydrophobic compounds (Skala et al., 2019). We hypothesized that high hydrophobicity of Res-TFN attributed to the abundance of aromatic groups would facilitate selective adsorption of CVOCs over 1,4-dioxane. In this study, TCE, 1,1-dichloroethylene (1,1-DCE), and cis-1, 2-dichloroethylene (cis-1,2-DCE) were chosen as target CVOCs compounds and their competitive adsorption in the presence of 1,4-dioxane was investigated using  $\beta$ -CD-HDI,  $\beta$ -CD-EPI and Res-TFN adsorbents. Furthermore, experiments were conducted to investigate the kinetics and isotherms of the adsorption process, aiming to gain a deeper understanding of the adsorption mechanism and determine the adsorption capacities.

## 2. Materials and methods

### 2.1. Synthesis

The synthesis of polymers including  $\beta$ -CD-EPI,  $\beta$ -CD-HDI, and  $\beta$ -CD-TFN was carried out following the methods outlined in the literature (Peixiao Tang, 2018; Shoji et al., 1996; Yamasaki et al., 2006), with minor modifications as noted below. The synthesis of resorcinarene crosslinked with TFN (Red-TFN) was carried out following the literature procedure of (Skala et al., 2019) with minor adjustments, also as noted below. Fourier transform infrared (FTIR) spectroscopy was utilized to identify and characterize the functional groups within the polymer, confirming the successful integration of desired monomers and functional groups during the polymerization process. The quality of the polymers was evaluated by comparing the spectrum to a reference spectrum and detecting any unexpected absorption peaks or shifts in peak positions. This information facilitated the optimization of the synthesis processes to minimize the formation of impurities. The results are depicted in Fig. S1-S4 and confirmed the successful synthesis of the desired polymers.

**2.1.1. Synthesis of  $\beta$ -CD-EPI**—A solution of 20% sodium hydroxide in 250 ml distilled water was prepared.  $\beta$ -CD (100 g) and EPI (152 g) were mixed in this solution at 50°C. The resulting mixture was slowly added to magnetically stirred liquid paraffin at 40°C. After allowing it to react overnight, the formed beads were separated from the liquid paraffin. The beads were then washed successively with hexane, acetone, and distilled water. Subsequently, the  $\beta$ -CD-EPI was dried under vacuum at 60°C for two days. Finally, it was rinsed with methanol and distilled water, followed by another round of vacuum drying at 60°C for two days.

**2.1.2. Synthesis of  $\beta$ -CD-HDI**—To synthesize  $\beta$ -CD-HDI, 2.0 g of  $\beta$ -CD was mixed with one drop of dibutyltin dilaurate and 15 ml of dimethylformamide (DMF). The mixture was stirred in a nitrogen atmosphere. A solution of 1.2 g HDI in 5 ml of DMF was prepared separately. The solution was added drop by drop to the mixture of  $\beta$ -CD and heated at 70 °C for 24 hours in a nitrogen atmosphere. The content of the flask, consisting of the  $\beta$ -CD polymer, was poured into chloroform. The resulting suspension was stirred, and the precipitate was collected through filtration. To remove any unreacted  $\beta$ -CD, it was rinsed with water. The solid was then collected through filtration and vacuum dried at 60°C.

**2.1.3. Synthesis of  $\beta$ -CD-TFN**—The synthesis of  $\beta$ -CD-TFN involved a chemical reaction where the hydroxyl groups in  $\beta$ -CD were replaced by TFN through nucleophilic aromatic substitution. The incorporation of numerous fluorinated groups was anticipated to enhance the hydrophobicity of  $\beta$ -CD-TFN, therefore facilitating the competitive adsorption of CVOCs in the presence of 1,4-dioxane. The procedure began by charging a dried 250 mL three-neck round bottom flask with  $\beta$ -CD (2.05 g, 1.81 mmol), TFN (1.00 g, 5.15 mmol), and  $K_2CO_3$  (3.2 g, 23.2 mmol). Subsequently, 50 ml of DMF was added, and the flask was purged with nitrogen gas. The mixture was then stirred at 80°C and 500 rpm for 15 hours. Afterward, the resulting suspension was filtered and gradually cooled to room temperature. The precipitate was washed with 0.5 N HCl, water, and DMF. Finally, the polymer was dried using a laboratory vacuum freezer.

**2.1.4. Synthesis of Res-TFN**—Resorcinarene (125 mg, 0.230 mmol) and TFN (91 mg, 0.46 mmol) were added to a 20 mL reaction vial. Anhydrous Dimethylsulfoxide (4 mL) was then added using a syringe. The vial was heated to dissolve the monomers completely. Once dissolved,  $K_2CO_3$  (636 mg, 4.60 mmol) was added, and the reaction was immediately placed in a preheated oil bath at 150°C. The reaction mixture was heated at 150°C for 3 hours and then cooled to room temperature. The resulting gel was pulverized using a spatula and filtered. The filtered gel was transferred to 50 mL of nanopure  $H_2O$ . 1 M HCl was slowly added until the pH reached a range of 1–3. The polymer was then stirred in acetone (100 mL) for 45 minutes. Subsequently, the polymer underwent continuous washing with hot methanol in a Soxhlet extractor, and finally, it was dried under vacuum for two days.

## 2.2. Characterization

FTIR analysis was conducted on all four adsorbents in this study, as illustrated in figures S1 to S4. Based on the initial batch removal experiments,  $\beta$ -CD-TFN and Res-TFN were selected as promising candidates and were subjected to further characterization (Fig 1). Figs 1a and 1c shows the chemical structures of Res-TFN and  $\beta$ -CD-TFN. The incorporation of numerous fluorinated groups was anticipated to enhance the hydrophobicity of  $\beta$ -CD-TFN, therefore facilitating the competitive adsorption of CVOCs in the presence of 1,4-dioxane.

The SEM image of RES-TFN (Hitachi S-4600) illustrated numerous irregularly shaped structures with varying sizes (Fig 1b). In contrast, the surface morphology of  $\beta$ -CD-TFN displayed distinctive porous characteristics (Fig 1d). The particle size distribution of Res-TFN was found to be bimodal with dominant sizes around 1 and 10  $\mu m$ . (Fig S5). Res-TFN involved a substitution reaction between TFN and resorcinarene, yielding a microporous solid polymer with a high internal surface area. The synthesis of  $\beta$ -CD-TFN involved crosslinking  $\beta$ -CD with rigid aromatic groups of TFN and led to solids with lower surface area. Res-TFN exhibited a Brunauer-Emmett-Teller surface area ( $S_{BET}$ ) of 914  $m^2 \cdot g^{-1}$ . (Fig. 1e), whereas  $\beta$ -CD-TFN showed an  $S_{BET}$  of 229  $m^2 \cdot g^{-1}$  (Fig. 1f) (Peixiao Tang, 2018).

## 2.3. Initial batch removal experiments

To assess the potential adsorption and selectivity of the adsorbents for the desired compounds (1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane) initial batch adsorption experiments were conducted with a contact time of 24 hours using a mixture of the target compounds with rotational mixing. The initial concentrations of the target compounds were set to 100  $\mu g \cdot L^{-1}$ , and the adsorbent dosage was 1  $g \cdot L^{-1}$ , except for AC, for which a dosage of 500  $mg \cdot L^{-1}$  was chosen. The performance of the adsorbents was evaluated against that of AC, which served as a benchmark. 12  $\times$  14 prewashed AC purchased from EnviroSupply & Service; Inc. was employed as the benchmark material. The AC was ground into a fine powder using a mortar and pestle. Based upon these initial batch studies, Res-TFN and  $\beta$ -CD-TFN were chosen for further kinetics and isotherm evaluation. The remaining sorbents showed minimal sorption of the target compounds (see Discussion).

## 2.4. Kinetics experiments

The kinetics experiments were carried out in 25 mL culture tubes with Teflon lining screw caps. A feed solution was prepared with an initial concentration of 100  $\mu g \cdot L^{-1}$  of each

contaminant, including 1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane. The dosage of Res-TFN was set at  $0.2 \text{ g}\cdot\text{L}^{-1}$ , while  $\beta$ -CD-TFN dosage was set at  $0.1 \text{ g}\cdot\text{L}^{-1}$ . For Res-TFN, seven samples were prepared at contact times of 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, and 6 h. However, for  $\beta$ -CD-TFN, longer time intervals were chosen due to its lower adsorption observed in the primary adsorption experiments. Samples were analyzed after 10 min, 30 min, 1 h, 2 h, 6 h, and 24 h of contact time. A rotating mixer was utilized to facilitate sample mixing throughout the experiments. Triplicate measurements of the initial concentration were taken, and the average concentration was used for further calculations.

Target compounds mass loss was calculated using a simple mass balance (eq. (1)).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where  $C_0$  ( $\mu\text{g}\cdot\text{L}^{-1}$ ) is the initial concentration and  $C_t$  ( $\mu\text{g}\cdot\text{L}^{-1}$ ) was the measured final concentration of the adsorbing compound at time  $t$ . Blanks without adsorbent were used to assess losses in the test vials. Average deviations from initial concentrations in blanks were 5% and 15% for cis-1,2-DCE and 1,1-DCE, respectively, but included both positive and negative deviations suggesting simply analytical variability. There were modest losses averaging about 9% of the more adsorbing TCE in the control samples, suggesting some evaporation or wall adsorption in these samples. No losses were observed in control samples of 1,4-dioxane. The average blank concentration was used to define  $C_0$  in the mass balance (1).

The amount of removed sorbate was then determined by the following equation:

$$q_t = \frac{C_0 - C_t}{C_A} \times 100 \quad (2)$$

where  $q_t$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of the chemical adsorbed on the solid phase at any time  $t$ (h);  $C_0$  ( $\mu\text{g}\cdot\text{L}^{-1}$ ) is the average concentration of sorbate in the samples of the adsorption experiments;  $C_t$  ( $\mu\text{g}\cdot\text{L}^{-1}$ ) is the concentration of sorbate in the liquid phase at any sample time  $t$ (h); and  $C_A$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the concentration of adsorbent.

## 2.5. Isotherm experiments

Isotherm experiments were conducted using Res-TFN and  $\beta$ -CD-TFN. For the  $\beta$ -CD-TFN experiments, a dosage of  $1 \text{ g}\cdot\text{L}^{-1}$  was used. The concentrations of 1,1-DCE, cis-1,2-DCE, and TCE in the feed solution were set at 25, 50, 100, 250, and  $500 \mu\text{g}\cdot\text{L}^{-1}$ . However, since the initial batch experiments showed no significant adsorption of 1,4-dioxane, its concentration was halved to keep the final concentrations within an acceptable range for analysis.

Considering that Res-TFN demonstrated better adsorption in the initial batch experiments, a dosage of  $0.5 \text{ g}\cdot\text{L}^{-1}$  was used for the isotherm experiments. The initial concentrations

of 1,1-DCE, cis-1,2-DCE, and TCE in the feed solution were set at 100, 200, 500, 1000, and 2000  $\mu\text{g}\cdot\text{L}^{-1}$ , while the concentration of 1,4-dioxane was set at half of the mentioned concentrations. Four samples were prepared for each concentration, with different contact times of 30 min, 1 h, 2 h, and 6 h. Control samples were also prepared without any adsorbent to assess losses and define initial concentrations for the mass balance.

## 2.6. Analytical methods

Analysis was performed using the Atomx Automated Sample Prep System coupled with an Agilent 7890A/5975 GC/MS with Triple Axis Detector. Calibration standards covering a range of 5 to 100  $\mu\text{g}\cdot\text{L}^{-1}$  was created in 40 mL vials designed for headspace analysis. An Internal Standard (IS) of 2000  $\mu\text{g}\cdot\text{mL}^{-1}$  1,4-Difluorobenzene solution in methanol was used as an internal standard for CVOCs and 2000  $\mu\text{g}\cdot\text{mL}^{-1}$  1,4-Dioxane-d8 was used as an internal standard for 1,4-dioxane. Calibration exhibited  $r^2$  of 0.999 and an average relative standard deviation of 5.12%. Method detection limits were estimated to be 5  $\mu\text{g}\cdot\text{L}^{-1}$ .

Adsorption samples were filtered using PES 0.45  $\mu\text{m}$  syringe filters and glass syringes. Then, they were transferred to 40 mL vials for analysis. To ensure accurate measurements, dilution factors ranging from 2 to 20 were applied, as needed, to keep the concentrations within an acceptable range for analysis. To ensure calibration accuracy, quality control (calibration check standard) samples and blank samples were included in every 8 samples.

## 3. Results and discussion

### 3.1. Initial batch experiments

Initial batch experiments were designed to evaluate which of the adsorbents showed the most promise for adsorbing the target compounds and an indication of their selectivity for the chlorinated solvents over 1,4-dioxane. Fig. 2 depicts the percentage removal of 1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane from a mixture using the different adsorbents:  $\beta$ -CD-EPI,  $\beta$ -CD-TFN, Res-TFN, and AC. Notably,  $\beta$ -CD-HDI did not exhibit any measurable removal of the target compounds and is not included in the figure.  $\beta$ -CD-EPI displayed measurable but minimal removal of 1,1-DCE, cis-1,2-DCE, and TCE, with only 3%, 3%, and 8% removal, respectively.  $\beta$ -CD-TFN exhibited modest removal percentages, with 13% for 1,1-DCE, 12% for cis-1,2-DCE, and 29% for TCE. However, it did not demonstrate any removal of 1,4-dioxane. Among different  $\beta$ -CD adsorbents in this study,  $\beta$ -CD-TFN exhibited higher adsorption of CVOCs. It has been suggested that  $\beta$ -CD-TFN has higher porosity and larger surface area compared to other  $\beta$ -CD adsorbents due to presence of numerous aromatic groups in its polymeric structure (Peixiao Tang, 2018). We also suggest that presence of fluorinated groups in this adsorbent intensifies the role of hydrophobic interactions and improves its overall removal of CVOCs compared to other  $\beta$ -CD adsorbents in this study.

Among the synthesized polymers, Res-TFN demonstrated the highest removal efficiency. It removed 80% of 1,1-DCE, 83% of cis-1,2-DCE, and 84% of TCE, while the removal of 1,4-dioxane was 37%. The removal efficiencies of Res-TFN were comparable to AC, which removed 86% of 1,1-DCE, 88% of cis-1,2-DCE, and 85% of TCE. However, AC

showed much lower selectivity by removing 72% of 1,4-dioxane compared to Res-TFN. Initial batch removal experiments demonstrate higher affinity of Res-TFN for CVOCs in the competitive adsorption of CVOCs and 1,4-dioxane. High porosity and enhanced hydrophobicity of Res-TFN resulting from the abundance of aromatic groups, can account for the increased adsorption of CVOCs compared to  $\beta$ -CD adsorbents in this study. Based upon these initial experiments, Res-TFN and  $\beta$ -CD-TFN were retained for kinetics and equilibrium isotherm testing although Res-TFN will be the focus of discussion given its better performance in magnitude of adsorption of the target compounds as well as selectivity toward the chlorinated solvents over 1,4-dioxane.

### 3.2. Adsorption kinetics

The preliminary batch removal studies were followed by kinetic experiments in which the amount adsorbed was monitored as a function of time under a specific set of conditions to assist in defining experimental times for more complete isotherm measurements. The time required to process samples suggested that a complete kinetics evaluation was not possible unless the overall kinetics were the order of hours or longer. Equilibrium adsorption of the target compounds with Res-TFN was achieved within 30 minutes of the initiation of an experiment (Fig 3). The kinetics of adsorption of  $\beta$ -CD-TFN were similar in that there was not a significant difference between adsorption at the first sampling point (10 minutes) versus the second (30 minutes). The rapid adsorption of the CVOCs was coupled with minimal adsorption of 1,4-dioxane.

### 3.3. Adsorption isotherm

Based upon the kinetic data, isotherm adsorption measurements were conducted at times from 30 minutes up to 6 hours when all measurements would be expected to be at equilibrium. Adsorption isotherm data were analyzed using the linear model and the Freundlich model, and the results are presented in Table 1 for  $\beta$ -CD-TFN and Table 2 for Res-TFN, respectively. Both adsorbents demonstrated a linear isotherm behavior within the concentration range of up to 2000  $\mu\text{g}\cdot\text{L}^{-1}$  for Res-TFN and 500  $\mu\text{g}\cdot\text{L}^{-1}$  for  $\beta$ -CD-TFN, respectively. Res-TFN exhibited higher adsorption capacities compared to  $\beta$ -CD-TFN. However, the adsorption capacity for 1,4-dioxane was insignificant for  $\beta$ -CD-TFN and barely quantifiable for Res-TFN.

The  $K_d$  values for Res-TFN were approximately one order of magnitude higher than those for  $\beta$ -CD-TFN. This could be explained by the higher surface area of Res-TFN compared to  $\beta$ -CD-TFN.  $S_{\text{BET}}$  of Res-TFN was measured 914  $\text{m}^2\cdot\text{g}^{-1}$  while the corresponding value for  $\beta$ -CD-TFN was 229  $\text{m}^2\cdot\text{g}^{-1}$ . Furthermore,  $\beta$ -CD-TFN demonstrated a larger pore size, classifying it as a mesoporous polymer, whereas Res-TFN exhibited microporous characteristics. On the other hand, pore size of  $\beta$ -CD-TFN is too big to retain CVOCs. Both Res-TFN and  $\beta$ -CD-TFN showed higher  $K_d$  values for TCE, indicating stronger adsorption, while the  $K_d$  values for 1,1-DCE and cis-1,2-DCE were 4–5 times lower. The estimated  $K_d$  values for TCE from the linear model were 9.75  $\text{L}\cdot\text{g}^{-1}$  for Res-TFN and 0.918  $\text{L}\cdot\text{g}^{-1}$  for  $\beta$ -CD-TFN. The higher adsorption capacities observed for TCE can be attributed to its higher hydrophobicity compared to the other chlorinated solvents. Notably the adsorption of 1,4-dioxane was approximately 2 orders of magnitude lower than TCE, indicating the



selectivity of the Res-TFN for the CVOCs.  $\beta$ -CD-TFN exhibited lower adsorption capacities compared to Res-TFN and measurements were subject to greater uncertainty due to the low adsorption. The adsorption of 1,4-dioxane onto  $\beta$ -CD-TFN was not statistically significantly different from 0 and therefore is not estimated in Table 1.

Individual Freundlich and linear fitted isotherms are compared to the measurements in the SI. The Freundlich fits to the isotherm data had minimal effects on  $R^2$  and residual error suggesting that the simpler linear model is perhaps most appropriate over the measured concentration range.

AC has been studied as an adsorbent for these target compounds by other researchers ((Ikuo et al., 1979; Jya-Jyun & Shinn-Yow, 2000)). The adsorption capacity of AC can be compared to Res-TFN by a simple ratio  $R_{qC} = \frac{q_{AC,C}}{q_{Res-TFN,C}}$  where C is the aqueous concentration at which the comparison is made (in  $\mu\text{g}\cdot\text{L}^{-1}$ ). Even if the adsorption into Res-TFN is linear, the adsorption onto AC is not and thus this ratio is a function of concentration. Table 3 contains value of this ratio for concentrations of 10 and 100  $\mu\text{g}\cdot\text{L}^{-1}$ .  $R_{q10}$  and  $R_{q100}$  are of order 1 for TCE, suggesting that both AC and Res-TFN have similar capacities for TCE. For 1,4-dioxane, however, the  $R_{q10}$  and  $R_{q100}$  are approximately 100 times bigger suggesting that 1,4-dioxane is not effectively adsorbed by Res-TFN. The large difference in adsorption of TCE relative to 1,4-dioxane is an indicator that Res-TFN can be used as a selective adsorbent to separate the CVOCs from 1,4-dioxane.

Fig 4 presents a comparison of  $\log q_t$  against  $\log C_e$  for Res-TFN and AC. The graph also indicates that Res-TFN and AC exhibit similar adsorption capacities for chlorinated solvents but show a substantial difference in their adsorption capacities for 1,4-dioxane with AC demonstrating a higher capacity for adsorbing 1,4-dioxane.

Fig 5 represents a correlation between  $\log K_d$  (Freunlich isotherm model) and  $\log K_{ow}$  for AC and Res-TFN. The graph suggests that hydrophobic interactions play a key role in Res-TFN adsorption mechanism. In the case of Res-TFN, an increase in the  $K_{ow}$  of target compounds corresponds to an increase in  $\log K_d$ . Conversely, for AC,  $\log K_d$  remains relatively consistent across different compounds, suggesting that hydrophobic interactions have a less important role in its adsorption process. The steeper slope in the Res-TFN graph highlights a stronger correlation between the hydrophobicity of target compounds and  $\log K_d$ . In contrast, the shallow slope in the AC graph suggests that hydrophobic interactions play a less important role in AC's adsorption behavior. This is the cause of the higher selectivity of Res-TFN compared to AC in a medium where both CVOCs and 1,4-dioxane are present.

#### 4. Conclusion

In this study, four different adsorbents were investigated for their selective adsorption of 1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane. Among the  $\beta$ -CD adsorbents,  $\beta$ -CD-HDI and  $\beta$ -CD-EPI showed negligible adsorption of CVOCs and 1,4-dioxane.  $\beta$ -CD-TFN demonstrated some adsorption of CVOCs but much less than Res-TFN which exhibited adsorption similar

to that expected of AC. Unlike AC, however, Res-TFN exhibited little adsorption for 1,4-dioxane, suggesting that it could be effectively used to separate CVOCs from 1,4-dioxane.

The adsorption isotherm behavior of both  $\beta$ -CD-TFN and Res-TFN was found to be linear within the range of concentrations examined. Res-TFN displayed higher adsorption capacities compared to  $\beta$ -CD-TFN, with the adsorption capacities following the order of TCE > cis-1,2-DCE > 1,1-DCE > 1,4-dioxane. This order of adsorption capacities is consistent with the hydrophobicity of the target compounds, indicating that the higher adsorption capacities for TCE can be attributed to its higher hydrophobicity. The difference in adsorption affinities between CVOCs and 1,4-dioxane suggests the potential of  $\beta$ -CD-TFN and Res-TFN for their separation.

Furthermore, the ratio of adsorption capacities of AC and Res-TFN indicates that Res-TFN exhibits much higher selectivity towards CVOCs allowing the CVOCs to be separated from 1,4-dioxane to aid in microbial degradation of the CVOCs.

We suggest a two-stage ex-situ column separation method for the treatment of a mixture of CVOCs and 1,4-dioxane in the real world. These columns will be packed with Res-TFN. In the initial phase, CVOCs are expected to be adsorbed in the first column, which then will be followed by applying anaerobic bacteria for a complete degradation of CVOCs. The outflow from the first column will then be directed to the second column, where 1,4-dioxane will be adsorbed to AC. An increased concentration of 1,4-dioxane in the second column will sustain biofilms consisting of a highly efficient culture to aerobically metabolize 1,4-dioxane. However, further research is necessary to identify how to design a practical separation and CVOCs degradation system around the Res-TFN. Res-TFN is likely to be more costly to prepare than AC, suggesting that separation and recycling of the Res-TFN is likely necessary.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgment

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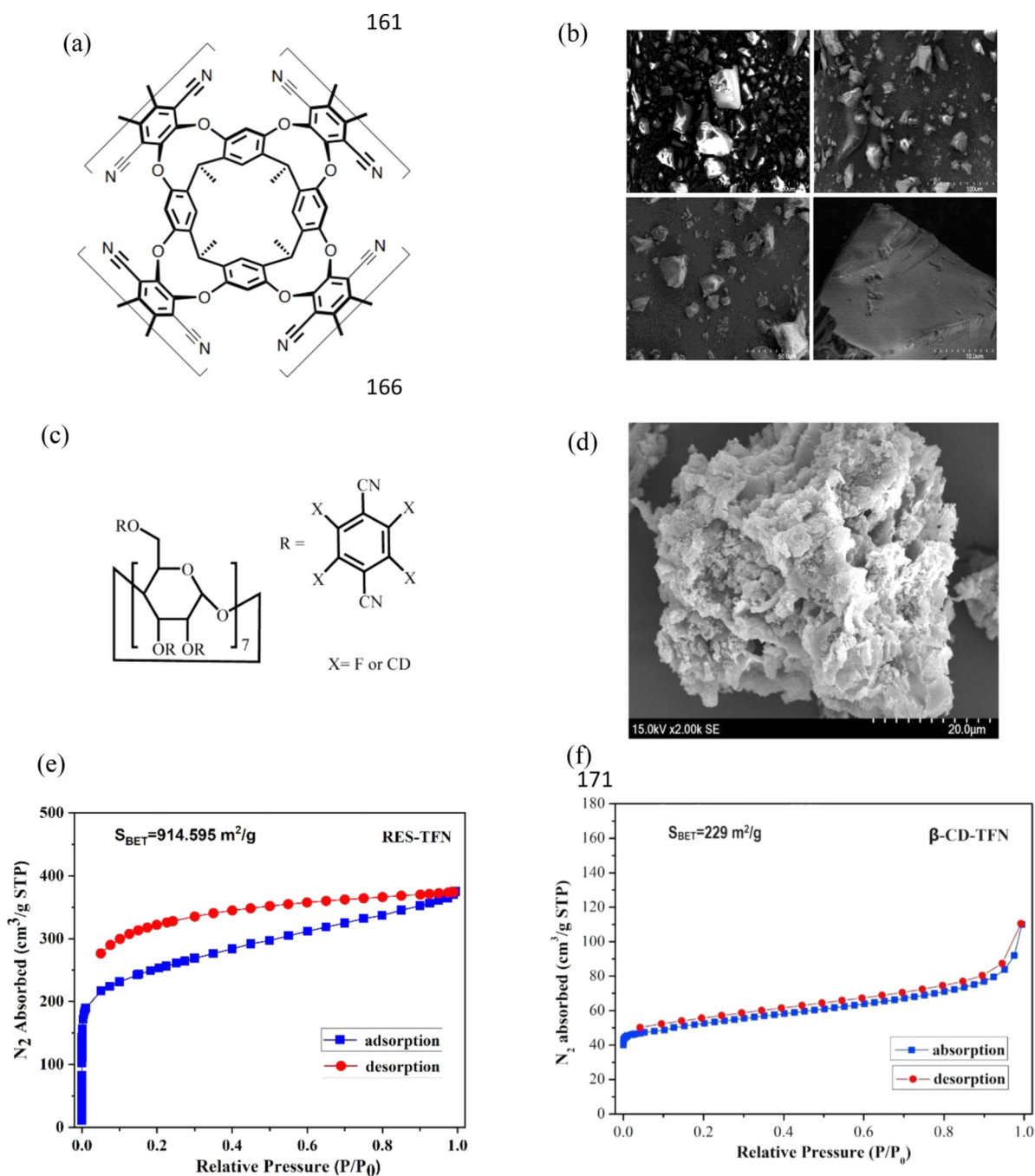
## Data availability

Data will be made available on request.

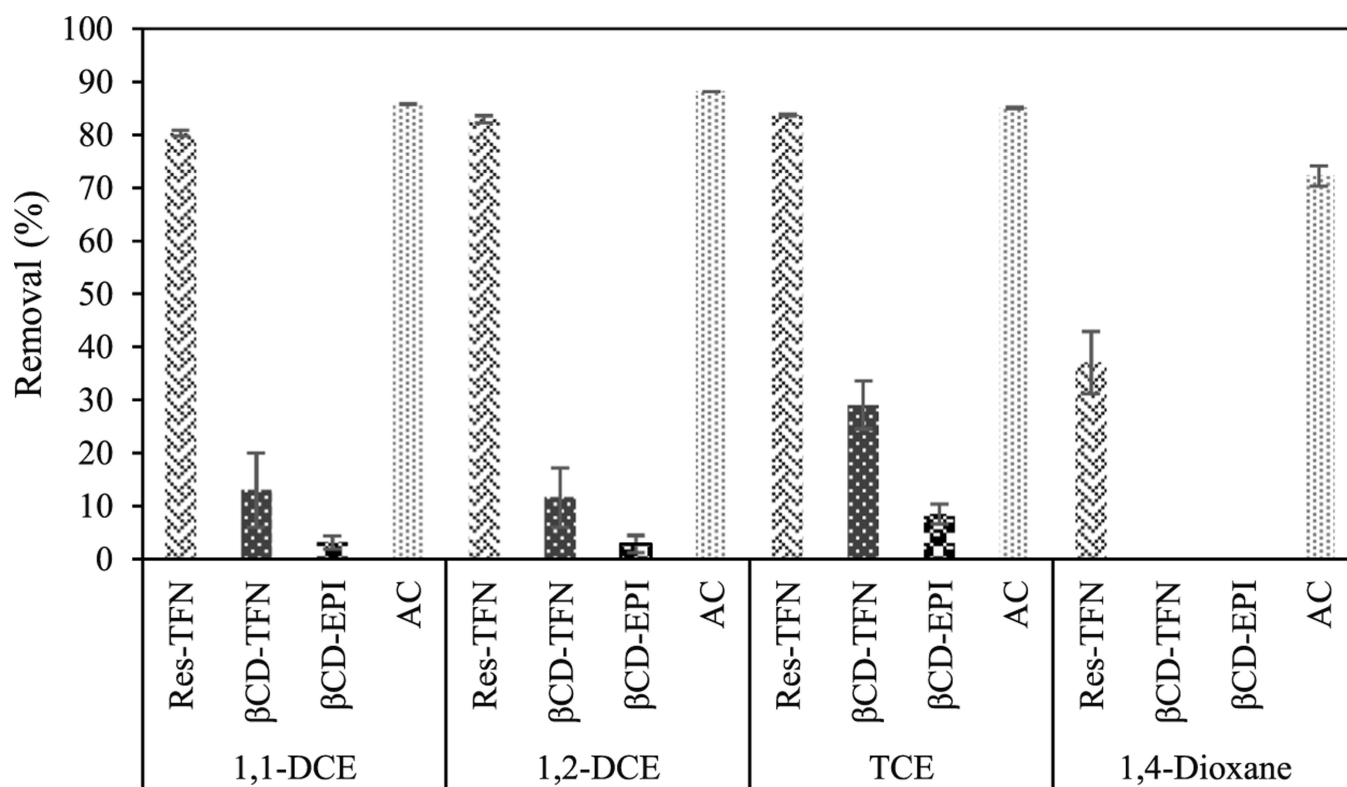
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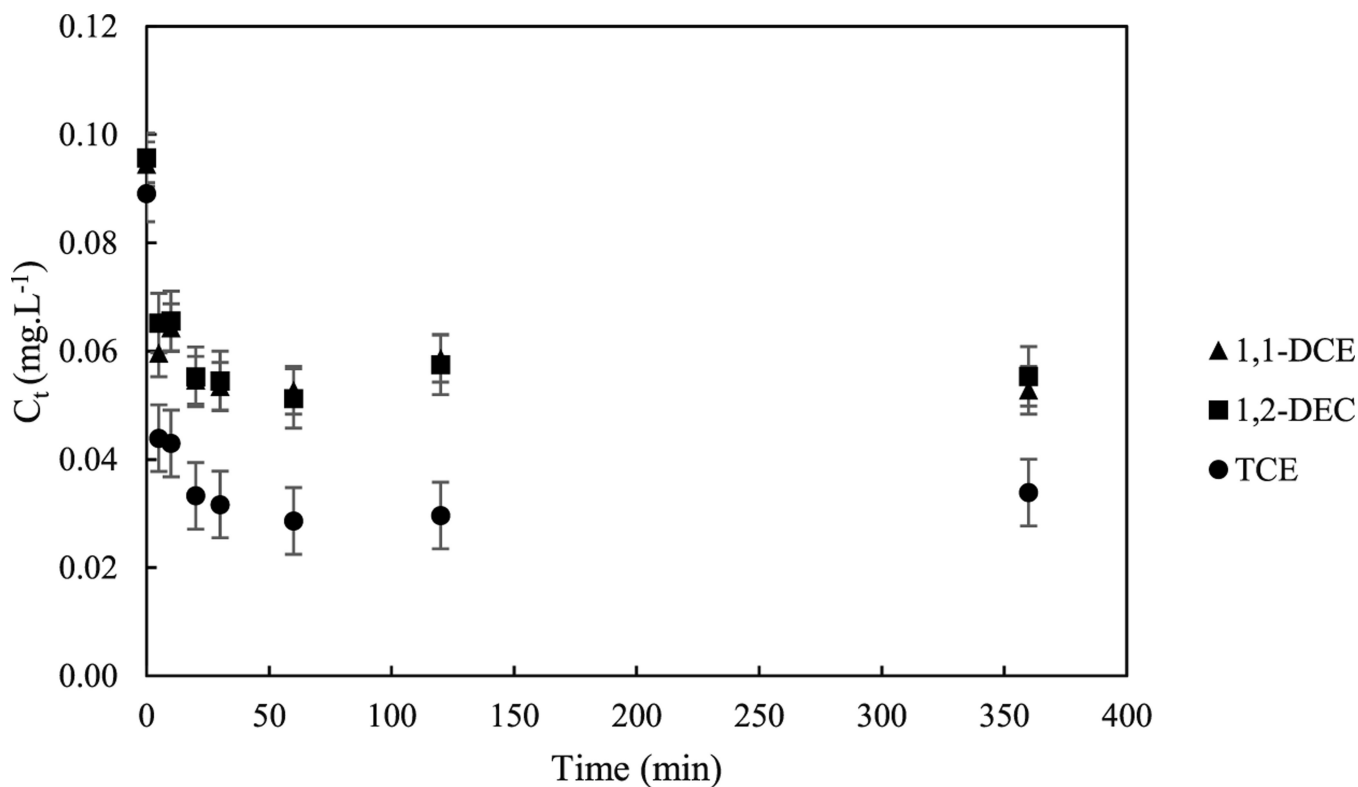
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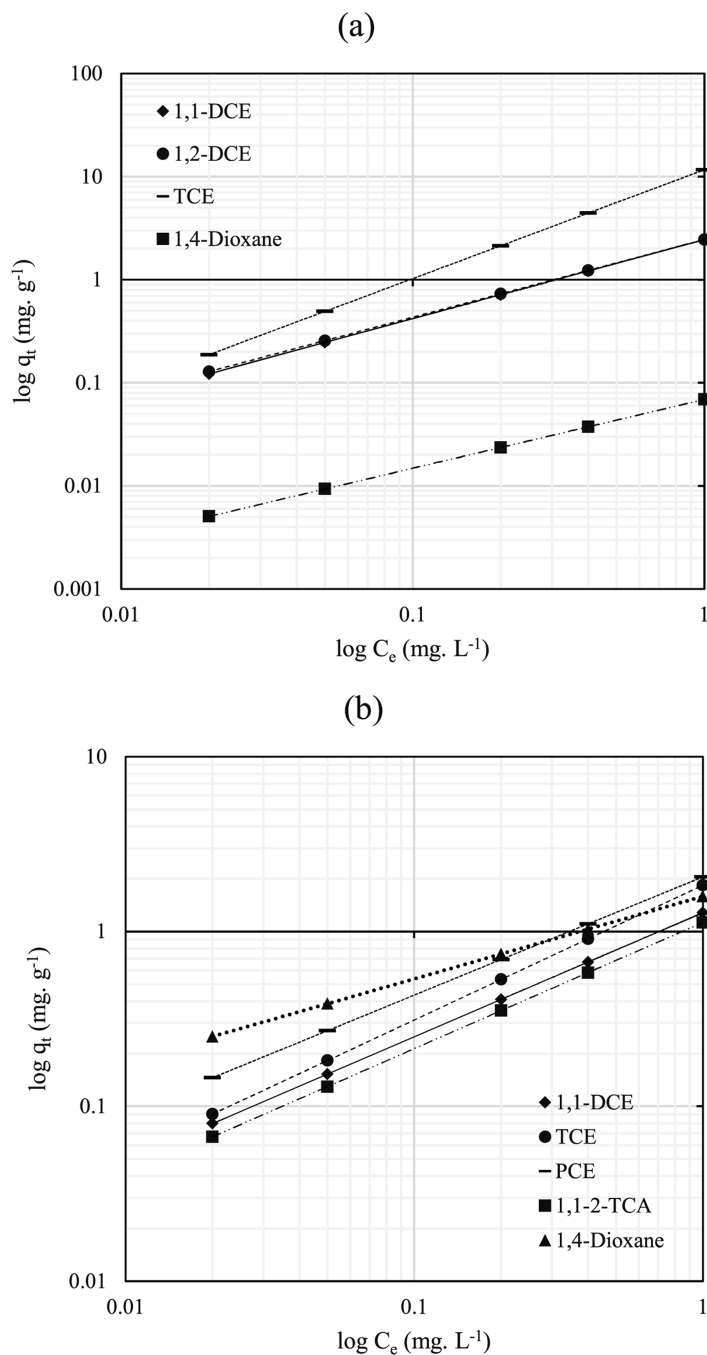
**Fig. 1.** Characterization of Res-TFN, and  $\beta$ -CD-TFN. (a) chemical structure of Res-TFN (b) SEM of Res-TFN (c) chemical structure of  $\beta$ -CD-TFN (d) SEM of  $\beta$ -CD-TFN (e) BET adsorption desorption of Res-TFN (f) BET adsorption desorption of  $\beta$ -CD-TFN. (d and f Reproduced with permission from Tang et al., 2018. Copyright 2018 Elsevier).



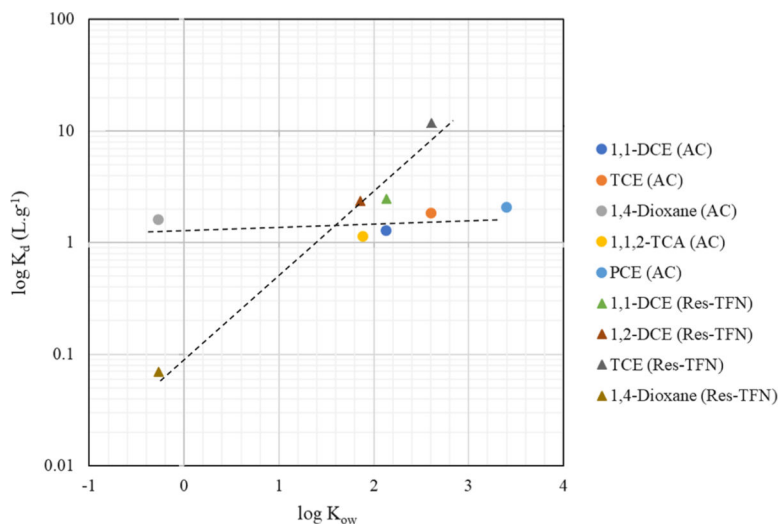
**Fig. 2.** Removal of 1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane using Res-TFN,  $\beta$ -CD-TFN,  $\beta$ -CD-EPI, and AC from an initial concentration of  $100 \mu\text{g}\cdot\text{L}^{-1}$  after 24 hours. The adsorbent  $\beta$ -CD-HDI was excluded from the analysis due to its lack of removal efficiency. Error bars in the graph represent the absolute error derived from triplicate measurements.



**Fig. 3.** Res-TFN adsorption kinetics of 1,1-DCE, cis-1,2-DCE, and TCE in a mixture of 100 µg·L<sup>-1</sup> containing 1,1-DCE, cis-1,2-DCE, TCE, and 1,4-dioxane. 1,4-dioxane was excluded from the kinetics plot since it did not exhibit any measurable adsorption. Error bars in the plot were determined based on the propagation of errors in the measurements of C<sub>0</sub> (initial concentration) and C(t) (concentration at time t).



**Fig. 4.**  $\log q_t$  vs.  $\log C_e$  for (a) Res-TFN and (b) AC. The data for AC was obtained from existing literature (Ikuro et al., 1979; Jya-Jyun & Shinn-Yow, 2000). Upon comparing the two graphs, it can be concluded that Res-TFN exhibits adsorption capacities that are similar to those of AC. On the other hand, AC exhibited significantly higher adsorption capacity for 1,4-dioxane, surpassing Res-TFN by more than an order of magnitude.



**Fig. 5.**  
 $\log K_d$  vs.  $\log K_{ow}$  of different compounds for AC and Res-TFN.



**Table 1**Isotherm parameters of  $\beta$ -CD-TFN

Compound	$K_d$ from linear fit (L. g <sup>-1</sup> )	R <sup>2</sup>	$K_d$ from power fit (C-mg. L <sup>-1</sup> )	R <sup>2</sup>
1,1-DCE	0.192	0.9888	0.229 (C) <sup>1.259</sup>	0.9986
cis-1,2-DCE	0.205	0.9986	0.222 (C) <sup>1.148</sup>	0.9981
TCE	0.918	0.9947	1.410 (C) <sup>1.198</sup>	0.9844
1,4-Dioxane	-	-	-	-

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**Table 2**

Isotherm parameters of Res-TFN

Compound	$K_d$ from linear fit (L. g <sup>-1</sup> )	R <sup>2</sup>	$K_d$ from power fit (C-mg. L <sup>-1</sup> )	R <sup>2</sup>
1,1-DCE	2.138	0.9745	2.455 (C) <sup>0.768</sup>	0.9947
cis-1,2-DCE	2.152	0.9819	2.359 (C) <sup>0.754</sup>	0.9981
TCE	9.752	0.9876	11.67 (C) <sup>1.056</sup>	0.9839
1,4-Dioxane	0.0831	0.8643	0.069 (C) <sup>0.668</sup>	0.8639

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**Table 3**Rq<sub>100</sub> and Rq<sub>10</sub> values for TCE and 1,4-dioxane

Compound	Rq <sub>10</sub>	Rq <sub>100</sub>
TCE	1.13	0.59
1,4-dioxane	89.24	56.83

\* q<sub>10</sub> and q<sub>100</sub> represent adsorption capacity at C<sub>e</sub>= 10 µg·L<sup>-1</sup> and C<sub>e</sub>= 100 µg·L<sup>-1</sup> respectively.

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